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Blending of additives with biodiesels to improve the cold flow properties, combustion and emission performance in a compression ignition engine—A review

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ABSTRACT

Biodiesel is widely accepted as comparable fuel to diesel in compression ignition engines. It offers many advantages including: higher cetane number; reduced emissions of particulates, NO_x, SO_x, CO, and hydrocarbons; reduced toxicity; improved safety; and lower lifecycle CO_2 emissions. A characteristic of biodiesel limiting its application is its relatively poor low-temperature flow properties. Improvement of its low temperature flow characteristic still remains one of the major challenges when using biodiesel as an alternative fuel for diesel engines. The biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds display higher cloud points and pour points thus limiting their applications.

The cold flow properties of different biodiesel were evaluated with various additives towards the objectives of improving the viscosity, pour point and cloud point. Methanol ethanol, kerosene, Mg additives, etc. have been tried many researchers to improve the cold flow behavior of biodiesels. Varying results of improvement in cold flow properties have been obtained by using different additives. Similarly different additives have been used by different researchers to improve the performance of a compression ignition engine and its emissions.

This review has been taken up to identify the various additives used to improve the cold flow properties of biodiesels and improve the performance of a diesel engine and its emissions while using additive blended biodiesels. The review concludes that the additives usage in biodiesel is inseparable both for improving the cold flow properties and for the better engine performance and emission control and further research is needed to develop biodiesel specific additives.

Contents

1. Introduction

The scarcity of conventional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs will make biomass sources more attractive [1]. Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are on the verge of reaching their peak production. The fossil fuel resources are shortening day by day. The scarcity of known petroleum reserves will make renewable energy sources more attractive [2]. Although majority of the renewable energy technologies are more eco-friendly than conventional energy options, their adoption is very slow because of various factors such as economic constraints, lack of supply, and technical know-how of users. Further the use of these technologies is still limited primarily to stationary operations, mainly due to technological limitations and poor economics [3]. The current alternative

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to diesel fuel can be termed to be biodiesel. Biodiesel can offer other benefits, including reduction of greenhouse gas emissions, regional development and social structure, especially to developing countries [4].

The usage of biofuels in compression ignition engine has been tried in both forms of straight vegetable oils and esters of vegetable oils or animal fats derived biodiesels with certain advantages and disadvantages of each. The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, and high price [5]. The effects of oxidative degradation caused by contact with ambient air (auto oxidation) during long-term storage present a legitimate concern in terms of maintaining the fuel quality of biodiesel [6]. A key property of biodiesel currently limiting its application to blends of 20% or less is its relatively poor low-temperature properties. Petroleum diesel fuels are plagued by the growth and agglomeration of paraffin wax crystals when ambient temperatures fall below the fuel's cloud point. These solid crystals may cause start-up problems such as filter clogging when ambient temperatures drop to around 10–15 °C [7]. While the cloud point of petroleum diesel is reported as 16 °C, biodiesel typically has a cloud point of around 0 °C, thereby limiting its use to ambient temperatures above freezing [8,9].

The biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher cloud points and pour points. The cloud point, which usually occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to the

the cloud point. Specifically, the removal of the double bonds on the ester group and the addition of a side-chain may provide a benefit in terms of low-temperature properties and offer improved oxidation stability. However, a negative impact on ignition quality and viscosity may result. Blending with petroleum diesel is only effective at low biodiesel proportions (up to 30 vol%) with cloud points to around 10 °C [9].

Several authors have published different works to improve the physical properties of biodiesels by the usage of different additives so that solve the problems associated physical properties of biodiesels for their large scale usage in diesel engines. A number of additives have been tried by different researchers for improving the combustion performance and also reduce emissions from diesel engines. A comprehensive review of these works is presented in this paper.

2. Improving the properties of vegetable oil

Vegetable oil has too high viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are a number of ways to reduce the viscosity of the vegetable oil. Dilution, micro-emulsification, pyrolysis and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. Chemical conversion of the oil to its corresponding fatty ester is called transesterification [12].

Following equation shows the transesterification reaction of triglycerides.

$$(H_2C-OCOR'1)(HC-OCOR'2)(H_2C-OCOR'3)\ Triglyceride + 3\,ROH\ Alcohol \xrightarrow{Catalyst} (ROCOR'1)(ROCOR'2)(ROC$$

formation of crystals and solidification of saturates. Crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons causes fuel starvation and operability problems as solidified material clog fuel lines and filters. With decreasing temperature more solids form and material approaches the pour point, the lowest temperature at which it will cease to flow. It has been well established that the presence of higher amount of saturated components increases the cloud point and pour point of biodiesel [10] utilization of additives (pour point depressants, anti-gel additives or cold flow improvers) that enhance the impact of crystal morphology; and blending with a fuel like kerosene which causes freezing point depression. Treatment with chemical additives is the most convenient and economical way of improving the low-temperature properties of diesel fuels. This technology is also very attractive in biodiesel industries. The chemical additives are generally referred to as pour point depressants, flow improvers or wax modifiers. Most additives promote the formation of small (10–100 mm) needle shaped crystals. These crystals experience significantly reduced growth and agglomeration rates as temperature decreases below cloud point. However, the rate of nucleation is promoted and causes the formation of a large quantity of the relatively small and more compact crystals. Although most of these crystals will be caught in fuel filters, the cake layer formed on the filter surface is considerably more permeable to fuel flow [11]. High viscosity leads to problem in pumping and spray characteristics (atomization and penetration, etc.). The inefficient mixing of oil with air contributes to incomplete combustion.

Several approaches have been proposed to improve the low-temperature properties of biodiesel, including: blending with petroleum diesel; the use of additives; and the chemical or physical modification of either the oil feedstock or the biodiesel product.

Additives designed for petroleum diesel have been used with limited success and specific additives for biodiesel remain in their infancy. The addition of branched moieties either to the alkyl head-group of the ester or as a side-chain to the tail-group can reduce

The biodiesel reaction requires a catalyst such as sodium hydroxide to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. The main byproduct is glycerin. The process reduces the viscosity of the end product. Transesterification is widely used to reduce vegetable oil viscosity [13]. It can be produced from oil from plants or from animal fats that are byproducts in meat processing. One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol (methanolysis) to make methyl esters of the straight chain fatty acid. The purpose of the transesterification process is to lower the viscosity of the oil. The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield [14].

Vegetable oils can be transesterified by heating them with a large excess of anhydrous methanol and a catalyst. The transesterification reaction can be catalyzed by alkalis [15,16], acids [17], or enzymes [18–22].

Attempts to influence the fatty acid profile of either the oil feedstock or the biodiesel product include winterisation and fractionation which reduce the fraction of saturated fatty acids and result in large reductions in yield. A reduction in saturated fatty acids reduces ignition quality of the fuel, while an increase in unsaturation reduces oxidation stability [6].

3. Improving the low-temperature properties of biodiesels

Several authors have published different works to improve the low-temperature properties of biodiesels by the usage of different additives for their convenient handling and usage at different climatic conditions.

Chiu and Schumacher Leon [23] reported that primary solutions to minimize bulk flow and fuel filter block problems include uti-

lization of fuel tank, fuel line and fuel filter heaters; utilization of additives (pour point depressants, anti-gel additives or cold flow improvers) that enhance the impact of crystal morphology; and blending with a fuel like kerosene which causes freezing point depression. According to them treatment with chemical additives is the most convenient and economical way of improving the low-temperature properties of diesel fuels. This technology is also very attractive in biodiesel industries. They observed that the chemical additives are generally referred to as pour point depressants, flow improvers or wax modifiers and most additives promote the formation of small (10–100 mm) needle shaped crystals. These crystals experience significantly reduced growth and agglomeration rates as temperature decreases below cloud point. However, the rate of nucleation is promoted and causes the formation of a large quantity of the relatively small and more compact crystals. Although most of these crystals will be caught in fuel filters, the cake layer formed on the filter surface is considerably more permeable to fuel flow.

Guru et al. [24] investigated the effect of magnesium based additive on the biodiesel physical properties pour point, viscosity and flash point of chicken fat methyl ester which is non corrosive in nature and has higher cetane number, but has certain disadvantages such as a high freezing point, high viscosity and high flash point. For this purpose magnesium based additive was synthesized stoichiometrically. They identified that increase in additive concentrations from 0 to 16 mmol/l resulted in lower freezing point, viscosity and flash point. A dosage of 16 mmol Mg into the chicken fat methyl ester caused a 7 °C pour point decrease and viscosity was decreased from 5.184 to 4.812 and the flash point was decreased from 129 °C to 122 °C. They concluded that these improvements support the idea that the catalytic cracking effect of the additive results in smaller chains of hydrocarbons.

Ethanol and methanol, as well as products derived from these alcohols, such as ethers, are under consideration as a component of the bio fuels. Several researchers all around the globe are working on ethanol and methanol mixing to the biodiesel fuels to overcome the problems of higher viscosity.

Fernando and Hanna [25] determined the relative compatibilities of ethanol, biodiesel, and diesel fuel. They revealed that ethanol–biodiesel–diesel (EB–diesel) fuel blend micro-emulsions were stable well below sub-zero temperatures and have shown equal or superior fuel properties to regular diesel fuel. Despite ethanol having a considerably lower energy value, cetane number, and lubricity value than biodiesel or diesel fuel alone, the heat of combustion and cetane numbers of the EB–diesel blends remained steady, without significant reduction. Barabas and Todorut [26] studied the key fuel properties of the biodiesel–diesel–ethanol blends and investigated that blends had the same or very close density and viscosity to standardized diesel fuel. The surface tensions of the blends were only 20% higher than that of diesel fuels. They concluded that the blends containing 5% ethanol had very close fuel properties compared to diesel fuel.

Tang et al. [27] studied the effect of natural and synthetic antioxidants on the oxidative stability of biodiesel. This study investigated the effectiveness of various natural and synthetic antioxidants [α-tocopherol (α-T), butylated hydroxyanisole (BHA), butyl-4-methylphenol (BHT), *tert*-butylhydroquinone (TBHQ), 2, 5-di-*tert*-butyl-hydroquinone (DTBHQ), ionol BF200 (IB), propylgallate (PG), and pyrogallol (PY)] to improve the oxidative stability of soybean oil (SBO-), cottonseed oil (CSO-), poultry fat (PF-), and yellow grease (YG-) based biodiesel at the varying concentrations between 250 and 1000 ppm. Their results indicated that different types of biodiesels had different natural levels of oxidative stability, indicating that natural antioxidants play a significant role in determining oxidative stability. Moreover, PG, PY, TBHQ, BHA, BHT, DTBHQ, and IB could enhance the oxidative stability for these different types of biodiesel. They also identified that antioxidant activity increased with increasing concentration. The induction period of SBO-, CSO-, YG-, and distilled SBO-based biodiesel could be improved significantly with PY, PG and TBHQ, while PY, BHA, and BHT showed the best results for PF-based biodiesel. They concluded that the effect of each antioxidant on biodiesel differs depending on different feedstock. Further they identified that the effect of antioxidants on B20 and B100 was similar; suggesting that improving the oxidative stability of biodiesel can effectively increase that of biodiesel blends. The oxidative stability of untreated SBO-based biodiesel decreased with the increasing indoor and outdoor storage time, while the induction period values with adding TBHQ to SBO-based biodiesel remained constant for up to 9 months.

Liang et al. [28] investigated the effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. They conducted experiments on the crude and distilled methyl esters of palm oil and found that crude palm oil has better oxidative stability. They attributed this to the presence of vitamin E (about 600 ppm), a natural antioxidant in the crude palm oil methyl esters. Natural and synthetic antioxidants were used in their study to investigate the effect on the oxidative stability of distilled palm oil methyl esters. It was found that both types of antioxidant showed beneficial effects in inhibiting the oxidation of distilled palm oil methyl esters. They found that the synthetic antioxidants were found to be more effective than the natural antioxidants as lower dosage (17 times less) was needed to achieve the minimum rancimat induction period of 6 h as required to meet the European standard for biodiesel (EN 14214).

Dunn [29] studied effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). This study examined the effectiveness of five such antioxidants, *tert*-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and α-tocopherol in mixtures with soybean oil fatty acid methyl esters (SME). Antioxidant activity in terms of increasing oxidation onset temperature (OT) was determined by non-isothermal pressurized-differential scanning calorimetry (P-DSC). Analyses were conducted in static (zero gas flow) and dynamic (positive gas flow) mode under 2000 kPa (290 psig) pressure and 5 °C/min heating scan rate. His results showed that PrG, BHT and BHA were most effective and α-tocopherol least effective in increasing OT. Increasing antioxidant loading (concentration) showed sharp increases in activity for loadings up to 1000 ppm followed by smaller increases in activity at higher loadings. He also conducted phase equilibrium studies to test physical compatibility of antioxidants in SME-No. 2 diesel fuel (D2) blends. Overall, this study recommends BHA or TBHQ (loadings up to 3000 ppm) for safeguarding biodiesel from effects of autoxidation during storage. BHT is also suitable at relatively low loadings (210 ppm after blending). PrG showed some compatibility problems and may not be readily soluble in blends with larger SME ratios. Although α-tocopherol showed very good compatibility in blends, it was significantly less effective than the synthetic antioxidants screened in this work.

Çaynak et al. [30] studied the production of biodiesel from pomace oil and improvement of its properties with synthetic manganese additive. They conducted tests by doping the additive with the methyl esters of pomace oil at a ratio of 12 μmol/l oil methyl ester. They found that led to a 20.37% decrease in viscosity, 7 °C fall in the flash point and reduced the pour point from 0 °C to −15 °C.

Keskin et al. [31] in their work 'Biodiesel production from tall oil with synthesized Mn and Ni based additives' studied the effect of Ni, Mn based metallic additives. Each metallic fuel additive was added at the rate of 8 μmol/l and 12 μmol/l to make mixtures of 60% tall oil methyl ester/40% diesel fuel (TE60) for preparing test fuels. They identified that metallic fuel additives improved properties of biodiesel fuels, such as pour point and viscosity values.

Kwanchareon et al. [32] in their work 'Solubility of a diesel–biodiesel–ethanol blend (diesohol), its fuel properties, and its emission characteristics from diesel engine' studied the phase diagram of diesel–biodiesel–ethanol blends at different purities of ethanol and different temperatures. They examined and compared fuel properties such as density, heat of combustion, cetane number, flash point and pour point of the selected blends and their emissions performance in a diesel engine to those of base diesel. They found that the fuel properties were close to the standard limit for diesel fuel; however, the flash point of blends containing ethanol was quite different from that of conventional diesel. The heating value of the blends containing lower than 10% ethanol was not significantly different from that of diesel. They concluded that a blend of 80% diesel, 15% biodiesel and 5% ethanol was the most suitable ratio for diesohol production because of the acceptable fuel properties except flash point.

Joshi et al. [33] improved the low-temperature operability, kinematic viscosity, and acid value of poultry fat methyl esters with addition of ethanol, isopropanol, and butanol.

They observed that the blends of ethanol in poultry fat methyl esters afforded the least viscous mixtures, whereas isopropanol and butanol blends were progressively more viscous, but still within specifications contained in ASTM D6751 and EN 14214. However they identified blends of alcohols in poultry fat methyl esters resulted in failure of the flash point specifications found in ASTM D6751 and EN 14214. Flash points of butanol blends were superior to those of isopropanol and ethanol blends, with the 5 vol% butanol blend exhibiting a flash point (57 °C) superior to that of No. 2 diesel fuel (52 °C). The most interesting observation is that blends of alcohols in poultry fat methyl esters resulted in an improvement in acid value with increasing content of alcohol. An increase in moisture content of biodiesel was observed with increasing alcohol content, with the effect being more pronounced in ethanol blends versus isopropanol and butanol blends. They did not observe any phase separation of alcohol–methyl esters samples at below the ambient temperatures.

Bhale et al. [11] evaluated the cold flow properties of Mahua methyl ester (Mahua biodiesel) with and without pour point depressants towards the objectives of identifying the pumping and injecting of these biodiesel in CI engines under cold climates. Effect of ethanol, kerosene and commercial additive on cold flow behavior of this biodiesel was studied. A considerable reduction in pour point has been noticed by using these cold flow improvers. Four concentrations of ethanol and kerosene blends, i.e. 5%, 10%, 15% and 20%, were tested with Mahua biodiesel for cold flow studies. To enhance the cold weather functionality of biodiesel fuel, the effect of commercial additive from Lubrizol (Lubrizol 7671) with the amount of 0.5%, 1%, 1.5% 2%, 2.5%, 3%, 3.5% and 4% was also studied. The reduction in cloud point of MME was from 291 K (18 °C) to 281 K (8 °C) when blended with 20% of ethanol and up to 278 K (5 °C) when blended with 20% of kerosene. Similarly the reduction in pour point was from 280 K (7 °C) to 269 K (−4 °C) when blended with 20% ethanol and up to 265 K (−8 °C) when blended with 20% kerosene. MME with 10% ethanol and 10% diesel reduces the pour point from 291 K (18 °C) up to 268 K (−5 °C). They concluded that ethanol and kerosene improve the cold flow properties MME when blended up to 20%. However, higher blends with ethanol are discouraged as it may reduce the overall calorific value. Also ethanol has very low value of cetane number. The various results obtained by them are shown as below [11].

Figs. 1 and 2 show the variation of kinematic viscosity in low-temperature region for MME, ethanol and kerosene blended MME. It can be clearly observed that the kinematic viscosity falls across all temperatures with the increase of percentage kerosene in the blend.

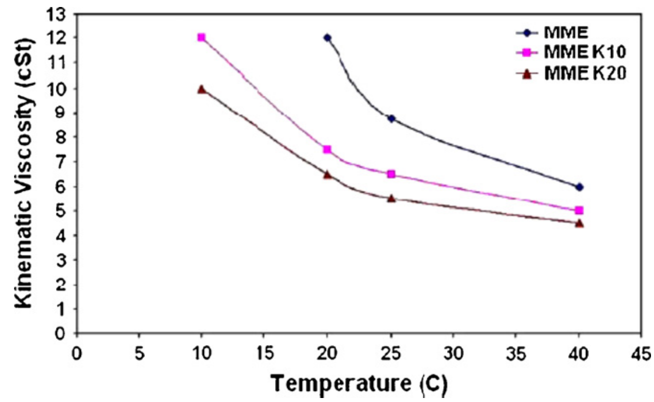

Fig. 1. Variation of kinematic viscosity of kerosene blended biodiesel (MME) in low-temperature region.

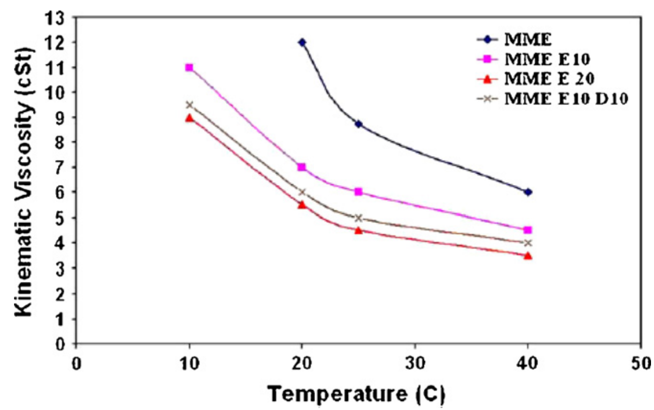

Fig. 2. Variation of kinematic viscosity (cSt) of ethanol blended biodiesel (MME) in low-temperature region.

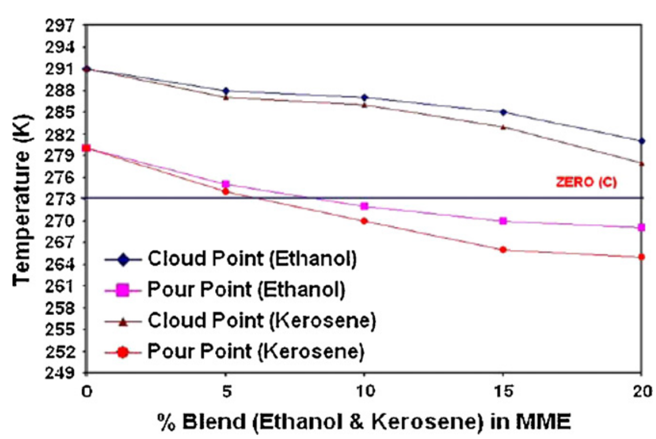

Fig. 3. Effect of ethanol and kerosene on cold flow properties of Mahua methyl ester.

Fig. 3 shows the reduction in pour point and cloud point of MME when blended with ethanol and kerosene. It can be seen from the figure that reduction in cloud point of MME by about 10 °C when blended with 20% of ethanol and up to 13 °C when blended with 20% of kerosene. Similarly the reduction in pour point was about 11 °C when blended with 20% ethanol and up to 15 °C when blended with 20% kerosene. MME with 10% ethanol and 10% diesel reduced the pour point by about 13 °C.

Fig. 4 shows the effect of Lubrizol additive on MME pour point. The MME pour point reduction by about 12 °C could be clearly seen when doped with Lubrizol up to 2%.

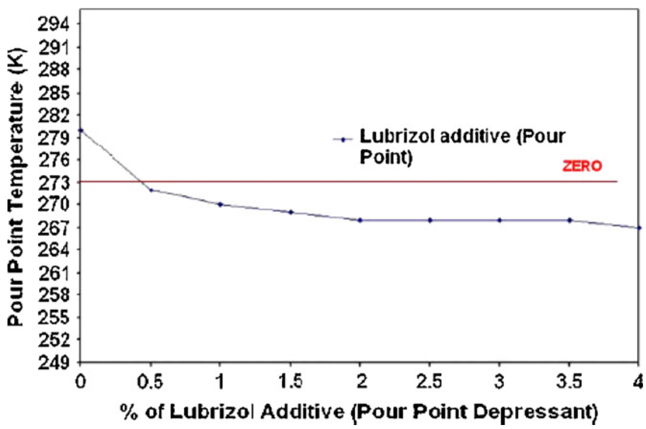

Fig. 4. Effect of Lubrizol additive (commercial pour point depressant) on MME.

4. Combustion performance and emission improvement

Many researchers have used different additives as a component of the biodiesels or blends of biodiesel fuels to improve either the combustion properties or improving the emission of a compression ignition engine. The additives used by different researchers include methanol, ethanol, di-ethyl ether, methyl oleate, synthetic Mg additives orange oil, kerosene, etc. Methanol can be produced from coal or petrol based fuels with low cost production, but it has very limited solubility in the diesel fuel. On the other hand, ethanol is a biomass based renewable fuel, which can be produced from vegetable materials, such as corn, sugar cane, sugar beets, sorghum, barley and cassava, and it has higher miscibility with diesel fuel [34]. Ethanol is a low cost oxygenate with high oxygen content (approximately 35%) that has been used in biodiesel–ethanol blends. It was reported [35] that the ethanol–diesel–biodiesel fuel blends are stable well below sub-zero temperature and have equal or superior fuel properties to regular diesel fuel

Ethanol and methanol, as well as products derived from these alcohols, such as ethers, are under consideration or in use as alternative fuels or as an additive biodiesel fuels. Methanol offers very low particulate emissions but the problems are their toxicity, low energy density, low cetane number, high aldehyde emissions, and harmful influence on materials used in engine production. Ethanol seems to be the best candidate as a sole fuel as a component of either gasoline or diesel oil [36]. Up till now ethanol was recognized only as a component of gasoline and not as a component of diesel oils. The properties of ethanol enable applying it also as a component of diesel oil. The potential of oxygenates as means of achieving zero net CO_2 renewable fuel, has resulted in considerable interest in the production and application of ethanol. In many countries such as the United States of America, Canada, Australia, Brazil, South Africa, Denmark, Sweden and others ethanol programs are realized. The research in ethanol programs is directed to identify factors that could influence engine performance and exhaust emissions. Understanding of these factors is necessary for the interpretation of the test results.

Keskin et al. [31] in their work ‘Biodiesel produced from tall oil synthesized with Mn and Ni based additives’ were tested in an unmodified direct injection diesel engine at full load condition. They found specific fuel consumption of biodiesel fuels increased by 6.00%, however, in comparison with 60% tall oil methyl ester/40% diesel fuel (TE60), it showed trend of decreasing with adding of additives. Exhaust emission profile of biodiesel fuels improved. CO emissions and smoke opacity decreased up to 64.28% and 30.91% respectively. They also observed low NO_x emission in general for the biodiesel fuels.

Kwanchareon et al. [32] studied the diesel–biodiesel–ethanol blends at different purities of ethanol and different temperatures. They found that CO and HC reduced significantly at high engine load, whereas NO_x increased, when compared to those of diesel. Taking these facts into account, a blend of 80% diesel, 15% biodiesel and 5% ethanol was the most suitable ratio for diesohol production because of the acceptable fuel properties (except flash point) and the reduction of emissions.

Lu et al. [37] studied on the detailed combustion characteristics and emissions of biodiesel-fueled engines with premixed ethanol by port injection. They carried out experiments on a single-cylinder, four-stroke, naturally aspirated direct injection engine at a fixed speed. From the heat release analysis they found that with the introduction of ethanol fuel by port injection, the ignition timing of the overall combustion event delayed remarkably, while the maximum heat release rate (HRR) increased smoothly. At a leaner fuel/air mixture, the peak value of the heat release rate increased slightly, the maximum in-cylinder gas pressure and temperature decreased, and the indicated thermal efficiency (ITE) deteriorated with the increase of ethanol proportion. While at a rich fuel/air mixture, with the increase of the ethanol proportion, the maximum HRR increases rapidly, the overall combustion event is completed at an earlier crank angle. They found the maximum values of the HRR reached the peak point in a certain premixed ratio which ranges from 20% to 40%. Also, the ITE reached the largest value at this operation point. When they introduced ethanol fuel by port injection, both the NO_x emission and smoke opacity decreased to a very low level under overall operation conditions. From their overall tests results they observed NO_x and smoke opacity simultaneously decreased about 35–85% compared to those of the neat biodiesel-fueled engines.

Kass et al. [38] tried water as an additive to lower NO_x and PM emissions in a light-duty diesel engine by using biodiesel-water emulsions with great success. In this study water was incorporated into neat biodiesel (B100) as an emulsion in an attempt to lower NO_x and particulate matter (PM) emissions. They formulated biodiesel emulsion containing 10 wt% water and evaluated against an ultra-low sulfur petroleum diesel (ULSD) and neat biodiesel (B100) in a light-duty diesel engine operated at 1500 rpm and 68 Nm. The influence of exhaust gas recirculation (EGR) was also examined. They identified that the incorporation of water was found to significantly lower the NO_x emissions while maintaining or improving fuel efficiency when operated the engine at 0% and 27% EGR, while the total PM mass was lowered dramatically for the 27% EGR condition only. From the analysis of the emissions and heat release data they concluded that the water enhances air-fuel premixing to maintain fuel economy and lower particulate matter.

Kass et al. [39] in an another work ‘Utilizing water emulsification to reduce NO_x and particulate emissions associated with biodiesel’ incorporated into neat biodiesel (B100) as an emulsion in an attempt to lower NO_x and PM emissions. A biodiesel emulsion containing 10 wt% water was formulated and evaluated against an ultra-low sulphur petroleum diesel and neat biodiesel (B100) in a light-duty diesel engine operated at 1500 rpm and at loads of 68 and 102 Nm (50 and 75 ft lbs). The influence of EGR was also examined by them. They observed that incorporation of water was found to significantly lower the NO_x emissions of B100 while maintaining fuel efficiency when operating at 0% and 27% EGR; however, NO_x emissions were observed to increase slightly for the emulsified fuel when the engine load was raised to 102 Nm. The soot fraction of the particulates (determined using an opacity meter) was much lower for the B100 and B100-water emulsion compared to the ULSD. In contrast, total PM mass (for the three fuel types) was unchanged for the 0% EGR condition but was significantly lower for the B100 and B100-emulsion during the 27% EGR condition compared to the

ULSD. They conclude from the analysis of the emissions and heat release data that the water enhances air-fuel premixing to maintain fuel economy and lower soot formation.

Zhu et al. [40] in their work 'Emissions characteristics of a diesel engine operating on biodiesel and biodiesel blended with ethanol and methanol' tested a 4-cylinder naturally aspirated direct-injection diesel engine with Euro V diesel fuel, pure biodiesel and biodiesel blended with 5%, 10% and 15% of ethanol or methanol. They conducted Experiments under five engine loads at a steady speed of 1800 rpm. They observed that compared with Euro V diesel fuel, the blended fuels could lead to reduction of both NO_x and PM of a diesel engine, with the biodiesel–methanol blends being more effective than the biodiesel–ethanol blends. The effectiveness of NO_x and particulate reductions was more effective with increase of alcohol in the blends. With high percentage of alcohol in the blends, the HC, CO emissions could increase and the brake thermal efficiency might be slightly reduced but the use of 5% blends could reduce the HC and CO emissions as well. They expect that with the diesel oxidation catalyst (DOC), the HC, CO and particulate emissions can be further reduced.

Shia et al. [41] worked on 'Emission reduction potential of using ethanol–biodiesel–diesel fuel blend on a heavy-duty diesel engine'. They described the emission characteristics of a three compounds oxygenated diesel fuel blend (EB-diesel), on a Cummins-4B diesel engine. EB-diesel is a new form of oxygenated diesel fuel blends consisted of ethanol, methyl soyate and petroleum diesel fuel. The blend ratio used in this study was 5:20:75 (ethanol:methyl soyate:diesel fuel) by volume. The results from the operation of diesel engine with EB-diesel showed a significant reduction in PM emissions and 2–14% increase of NO_x emissions. The change of CO emission was not conclusive and depended on operating conditions. They observed that total hydrocarbon from EB-diesel was lower than that from diesel fuel under most tested conditions. They measured formaldehyde, acetaldehyde, propionaldehyde and acetone in the exhaust and the results indicated that use of EB-diesel led to a slight increase of acetaldehyde, propionaldehyde and acetone emissions. They also detected a small amount of ethanol in the exhaust from burning EB-diesel.

Cheung et al. [42] carried out experiments on 'Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol' on a diesel engine operating on Euro V diesel fuel, pure biodiesel and biodiesel blended with methanol. The blended fuels contain 5%, 10% and 15% by volume of methanol. Experiments were conducted under five engine loads at a steady speed of 1800 rpm to assess the performance and the emissions of the engine associated with the application of the different fuels. The results indicated an increase of brake specific fuel consumption and brake thermal efficiency when the diesel engine was operated with biodiesel and the blended fuels, compared with the diesel fuel. They expect that the blended fuels could lead to higher CO and HC emissions than biodiesel, higher CO emission but lower HC emission than the diesel fuel. They also observed simultaneous reductions of NO_x and PM to a level below those of the diesel fuel. Regarding the unregulated emissions, compared with the diesel fuel, the blended fuels generate higher formaldehyde, acetaldehyde and unburned methanol emissions, lower 1,3-butadiene and benzene emissions, while the toluene and xylene emissions not significantly different.

Rahimi et al. [43] used diesterol: a mixture of fossil fuel diesel (D) sun flower oil methyl ester called biodiesel (B) and bioethanol produced from potato waste (E). They observed that adding oxygenated compounds to the new blend seems to slightly reduce the engine power and torque and increased the average specific fuel consumption for various speeds. Their experimental measurement and observation of smoke concentration, NO_x, CO and HC concentration indicated that both of these pollutants reduced by increasing the biofuel composition of diesterol throughout the engine operating range.

Labecka and Slavinskas [44] in their study of exhaust emissions of direct injection diesel engine operating on ethanol, petrol and rapeseed oil blends conducted tests on a four stroke, four cylinder, direct injection, unmodified, diesel engine operating on pure rapeseed oil (RO) and its 2.5 vol%, 5 vol%, 7.5 vol% and 10 vol% blends with ethanol (ERO), petrol (PRO) and both improving agents were applied in equal proportions as 50:50 vol% (EPRO).

They identified the biggest NO_x emissions, 1954 and 2078 ppm, at 2000 min^{-1} speed generated by blends PRO10 (9.72%) and EPRO5 (11.13%) against, 1731 and 1411 ppm, produced from ERO5 (12%) and ERO10 (13.2% oxygen) blends. The carbon monoxide, CO, emissions emitted from a fully loaded engine fuelled with three agent blends EPRO5–7.5 at maximum torque and rated speed are higher by 39.5–18.8% and 27.5–16.1% and smoke opacity were lower by 3.3–9.0% and 24.1–17.6% comparing with RO case. When operated at rated 2200 min^{-1} mode, they observed that the carbon dioxide, CO_2, emissions were lower, 6.9–6.3 vol%, from blends EPRO5–7.5 relative to that from RO, 7.8 vol%, accompanied by a slightly higher emission of unburned hydrocarbons HC, 16 ppm, and residual oxygen contents O_2, 10.4–12.0 vol%, in the exhaust.

Chen et al. [45] conducted similar tests as of Labecka and Slavinskas [44] on combustion characteristics and PM emission of diesel engines using ester–ethanol–diesel blended fuels.

In this study, vegetable methyl ester was added to ethanol–diesel fuel to prevent the separation of ethanol from diesel; thus the ethanol percentage can be up to 30% in volume. More attention was paid to its combustion characteristics, the effects of ethanol on PM components, soluble organic fraction (SOF), dry soot (DS), and sulfate mass, using different fuel blends in the engine. To understand the effect of ethanol blended diesel fuels on combustion processes and soot formation, images of combustion processes were recorded using a high-speed CCD camera. They identified that with the increasing ethanol in the blended fuel, both smoke and PM can be reduced, but the PM decrease was not as efficient as the smoke decrease. They observed that increasing ethanol in the fuel blend, the DS emission in PM reduced significantly, the sulfate emission hardly changed, and the SOF emission in PM was not reduced as expected. The results also indicate that addition of ethanol to diesel fuels the ignition is prolonged, maximum heat release ratio and peak pressure increase, and combustion duration is shortened. In addition, they found that flame luminosity in the combustion was decreased when using blended fuels, which indicated that soot formation in fuel-rich regions is suppressed by the ethanol.

Panga et al. [46] investigated the 'Characteristics of carbonyl compounds emission from a diesel-engine using biodiesel–ethanol–diesel as fuel' in a Cummins-4B diesel engine.

They identified that the biodiesel–ethanol–diesel operation resulted in higher total carbonyls emissions up to 1–12% than those from diesel fuel depending on engine operating conditions. They found that total carbonyls emission was in positive correlation with the engine speed. During the constant speed/varying load tests, minimum total carbonyls emission was found at 50% load. Compared with fossil diesel, the EB-diesel was observed to significantly reduce PM emission and increase slightly NO_x emission.

Cheng et al. [47] compared emissions of a direct injection diesel engine operating on biodiesel with emulsified and fumigated methanol. Experiments were performed on a 4-cylinder naturally aspirated direct injection diesel engine operating at a constant speed of 1800 rpm with five different engine loads. This study compared the effect of applying a biodiesel from waste cooking oil with 10% blended methanol and 10% fumigation methanol. The results indicate a reduction of CO_2, NO_x, and particulate mass emissions and a reduction in mean particle diameter, in both cases, compared

with diesel fuel. For the blended mode, they found a slightly higher brake thermal efficiency at low engine load while the fumigation mode gave slightly higher brake thermal efficiency at medium and high engine loads. In the fumigation mode, an extra fuel injection control system was required, and there was also an increase in CO, HC and NO_2 (nitrogen dioxide) and particulate emissions in the engine exhaust, which are disadvantages compared with the blended mode.

Kim and Choi [48] studied the effect of biodiesel and bioethanol blended diesel fuel on nanoparticles and exhaust emissions from CRDI diesel engine. They studied the characteristics of the particle size distribution, the reaction characteristics of nanoparticles on the catalyst, and the exhaust emission characteristics when a common rail direct injection (CRDI) diesel engine is run on biofuel-blended diesel fuels. The biofuel used was mixture of biodiesel, bioethanol. They observed that the engine performance under a biofuel-blended diesel fuel was similar to that under diesel fuel, and the high fuel consumption was due to the lowered calorific value that ensued from mixing with biofuels and the use of a biodiesel–diesel blend fuel reduced the total hydrocarbon and carbon monoxide emissions but increased nitrogen oxide emissions due to the increased oxygen content in the fuel. The smoke emission was reduced by 50% with the use of the bioethanol–diesel blend. They also observed that the use of biofuel-blended diesel fuel reduced the total number of particles emitted from the engine; however, the use of biodiesel–diesel blends resulted in more emissions of particles that were smaller than 50 nm, when compared with the use of diesel fuel. They concluded that the use of a mixed fuel of biodiesel and bioethanol (BD15E5) was much more effective for the reduction of the particle number and particle mass, when compared to the use of biodiesel 20% with diesel fuel.

Senthil Kumar et al. [49] in their work on different methods to improve the performance of a Jatropha oil fueled diesel engine tried neat Jatropha oil and methyl ester of Jatropha oil, dual fuel operation with Jatropha oil as the injected fuel and methanol, orange oil, and hydrogen as the inducted fuel, blends of Jatropha oil with methanol and orange oil, and use of oxygenates like diethyl ether and di-methyl carbonate as additives to Jatropha oil. The optimum results obtained with different methods have been compared. The comparison has been made at peak power output. They found an improvement in brake thermal efficiency with all methods as compared with neat Jatropha oil operation. Highest brake thermal efficiency was obtained in the dual fuel operation as compared with other methods. Brake thermal efficiencies obtained them were 30.7% with methanol, 29.4% with orange oil, and 29.3% with hydrogen in the dual fuel mode. The best energy shares found by them were 46% with methanol, 31% with orange oil, and 18% with hydrogen.

They also noted that with methanol induction the brake thermal efficiency was even better than neat diesel operation at the optimum energy share. Methyl ester of Jatropha oil also showed a higher thermal efficiency as compared with neat Jatropha oil and blends with methanol and orange oil. The methyl ester of Jatropha oil has lower viscosity, which results in better atomization of the fuel as compared with neat Jatropha oil. Methanol blend shows higher thermal efficiency (28.5%) than the orange oil blend (28.3%) due to superior physical characteristics of methanol than orange oil such as low viscosity (0.6 cp) and high vapor pressure (126 mm Hg at 30 °C). They identified that smoke reduced with all methods when compared with neat Jatropha oil. Greatest reduction in smoke emission was found in the dual fuel operation than the other methods. The homogeneous combustion of methanol and orange oil air mixture in the case of the dual fuel mode lowered the smoke level. The lowest smoke level (2.6 BSU) is obtained with methanol Jatropha oil dual fuel operation. Blends of methanol and orange oil also showed lower smoke levels than neat Jatropha oil. Methanol blend showed more reduction than orange oil due to increased premixed combustion rate as a result of increased ignition delay.

Many facts were also observed with regards to the combustion of various methods used in the experiments. Ignition delay was higher with neat Jatropha oil. It increased further with the blend and in dual fuel operation. It was reduced with the ester. Peak pressure and rate of pressure rise were higher with all the methods compared to neat Jatropha oil operation. Jatropha oil and methyl ester showed higher diffusion combustion compared to standard diesel operation. However, dual fuel operation resulted in higher premixed combustion. On the whole they concluded that transesterification of vegetable oils and methanol induction can significantly enhance the performance of a vegetable oil fuelled diesel engine.

Labeckas and Slavinskas [50] experimented on the influence of fuel additives on performance of direct-injection diesel engine and exhaust emissions when operating on shale oil. Tests were conducted by them on a naturally aspirated four stroke, four cylinder, water cooled, direct injection diesel engine when running on shale oil that has been treated with multi-functional fuel additives viz. Marisol FT (Sweden) and SO-2E (Estonia).

The purpose of their research was to evaluate the effectiveness of the fuel additives Marisol FT (Sweden) and SO-2E (Estonia) as well as to verify their ability to increase energy conversion and reduce brake specific fuel consumption, contamination and smoke opacity of the exhausts when fuelling the diesel engine with shale oil. Their test results showed that the application of these additives could be a very efficient means to improve diesel engine performance on shale oil, especially when operating at the light load range. The identified brake specific fuel consumption at light loads and speeds of 1400–2000 min^{-1} reduces by 18.3–11.0% due to the application of the Marisol FT. The additive SO-2E also produced nearly the same effect. The total NO_x emission from the fully loaded diesel engine fuelled with the treated shale oil reduced by 29.1% (SO-2E) and 23.0% (Marisol FT). Their test results showed that the CO emission at rated power increased by 16.3% (SO-2E) and 48.0% (Marisol FT), whereas the smoke opacity of the exhausts increased by 35% and over 2 times, respectively. However, the test results were complicated and ambiguous on the effect of the fuel additives on the HC emission.

Szybist et al. [51] worked on the evaluation of formulation strategies to eliminate the biodiesel NO_x effect. This was accomplished by spiking a conventional soy-derived biodiesel fuel with methyl oleate or with cetane improver. The conventional B20 blend produced a NO_x increase of 3–5% relative to petroleum diesel, depending on injection timing. However, when they used a B20 blend where the biodiesel portion contained 76% methyl oleate, the biodiesel NO_x effect was eliminated and a NO_x neutral blend was produced. Increasing the methyl oleate portion of the biodiesel to 76% also had the effect of increasing the cetane number from 48.2 for conventional B20 to 50.4, but this effect is small compared to the increase to 53.5 achieved by adding 1000 ppm of 2-ethylhexyl nitrate (EHN) to B20. They identified that for the particular engine tested, NO_x emissions were found to be insensitive to ignition delay, maximum cylinder temperature, and maximum rate of heat release. The dominant effect on NO_x emissions was the timing of the combustion process, initiated by the start of injection, and propagated through the timing of maximum heat release rate and maximum temperature.

Guru et al. [24] studied the effect organic based synthetic Mg additive with chicken fat based biodiesel in a single cylinder direct injection diesel engine. The additive was doped into the biodiesel blend by 12 μmol Mg. Engine tests were carried out with diesel fuel (EN 590) and a blend of 10% chicken fat biodiesel and diesel fuel (B10) at full load operating conditions and different engine speeds from 1800 to 3000 rpm. The results showed that, the engine torque

was not changed significantly with the addition of 10% chicken fat biodiesel, while the specific fuel consumption increased by 5.2% due to the lower heating value of biodiesel. In-cylinder peak pressure slightly rose and the start of combustion was earlier. CO and smoke emissions decreased by 13% and 9% respectively, but NO_x emission increased by 5%.

Shi et al. [52] made efforts to reduce NO_x and PM emissions from a diesel engine using both ethanol-selective catalytic reduction (SCR) of NO_x over an Ag/Al_2O_3 catalyst and a biodiesel–ethanol–diesel fuel blend on an engine test bench. They observed that use of EB-diesel increased PM emissions by 14% due to the increase in the soluble organic fraction of PM, but it greatly reduced the Bosch smoke number by 60–80% according to the results from 13-mode test of European Stationary Cycle test. They found that the SCR catalyst was effective in NO_x reduction by ethanol, and the NO_x conversion was approximately 73%, the total hydrocarbons and CO emissions increased significantly during the SCR of NO_x process. They used two diesel oxidation catalyst assemblies after Ag/Al_2O_3 converter to remove CO and HC. The PM composition analysis revealed that the net effect of oxidation catalyst on total PM was an integrative effect on SOF reduction and sulfate formation of PM. They concluded that the engine bench test results indicated that the combination of EB-diesel and a SCR catalyst assembly could provide benefits for NO_x and PM emissions control even without using diesel particle filters.

Chen et al. [53] used a bio-solution additive to reduce reducing emissions of both polycyclic aromatic hydrocarbons (PAHs) and PM from diesel engines. They found that when compared with P0 (premium diesel fuel as base fuel), E16P20 fuel (16 vol% bio-solution + 20 vol% palm-biodiesel + 64 vol% P0, an additional 1 vol% surfactant) saved 12.4% fuel consumption and reduced emissions of PM by 90.1%, total PAHs by 69.3%, and total BaPeq (benzo[a]pyrene equivalent concentration) by 69.6%. They concluded that the emulsified palm-biodiesel with bio-solution can be considered as a clean and alternative fuel.

McCormick et al. [54] in their experiments tested the additives di-*tert*-butyl-peroxide (DTBP) and 2-ethyl-hexyl-nitrate (EHN), short chain fatty acid esters, *tert*-butyl-hydroquinone (TBHQ, a food antioxidant), and a proprietary additive called A1 provided by Bio-Clean Fuels. They concluded that the cetane improvers DTBP and EHN are effective in reducing NO_x by 4% in B20 blends. DTBP is also effective at NO_x reduction for B100 fuels but not in proportion to the NO_x reduction observed for B20 blends. They observed that cetane improvers act largely to lower the NO_x produced during burning of the petroleum diesel fuel. The antioxidant TBHQ significantly reduced NO_x but also caused a small increase in particulate matter.

Bhale et al. [11] conducted experiments on four stroke water cooled single cylinder compression ignition engine and obtained the performance and emission with various blends of Mahua methyl ester (MME) with ethanol and diesel in various proportions. The results obtained by them showed that of diesel–ethanol blended MME had similar performance at part load and superior performance at full load to that of the diesel.

They obtained an average CO% reduction in 20% ethanol blended biodiesel over diesel was as high as 50%, reduction HC emission for ethanol blended biodiesel (E20 and E10) was lower than 9.15% and 5.25%, respectively, the ethanol blended biodiesel has shown low NO_x emission and was lowest for MME E20 blend, smoke emissions were lower 20% ethanol blended biodiesel. The results obtained by them are shown in the following graphs [11].

The variation of brake thermal efficiency with respect to load for different fuels considered for the present analysis is presented in Fig. 5. The brake thermal efficiency of diesel was almost highest from part load to full load on the other hand MME has the lowest value. This is mainly because of higher viscosity of MME as compared to diesel. Diesel–ethanol blended biodiesel have good performance at part load and superior performance at full load to that of the diesel.

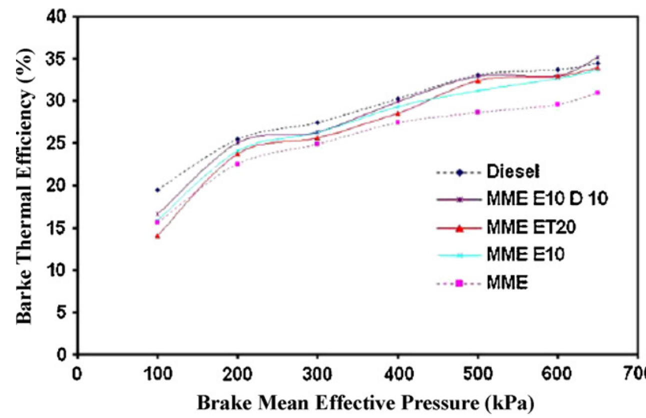

Fig. 5. Brake thermal efficiency for ethanol blended biodiesel.

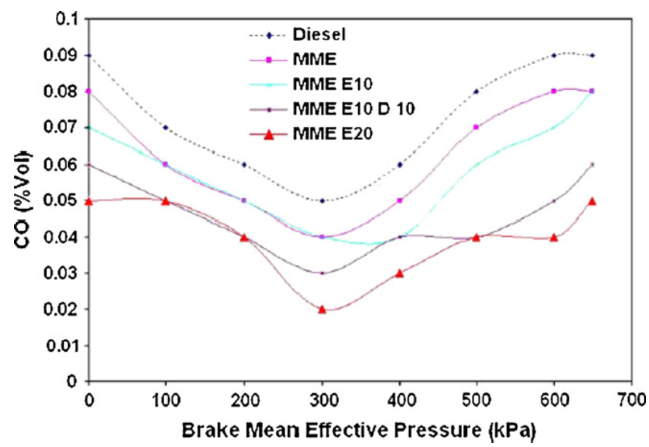

Fig. 6. CO emission for ethanol blended biodiesel.

Fig. 6 shows the plot of carbon monoxide emission of Mahua biodiesel and its various blends with ethanol at the rated engine speed of 1500 rpm at various load conditions. CO emission is higher for diesel as compared to biodiesel (MME) and ethanol blended biodiesel. The reduction in CO emission level with the addition of oxygenates (ethanol) is obvious. The average CO% reduction in 20% ethanol blended biodiesel over diesel was observed to be as high as 50%.

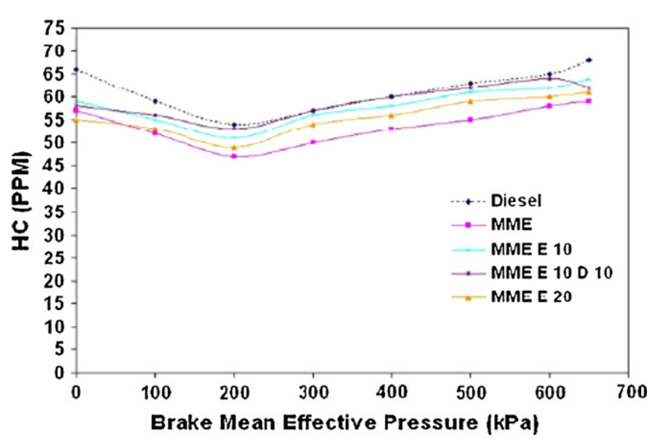

Fig. 7. HC emission for ethanol blended biodiesel.

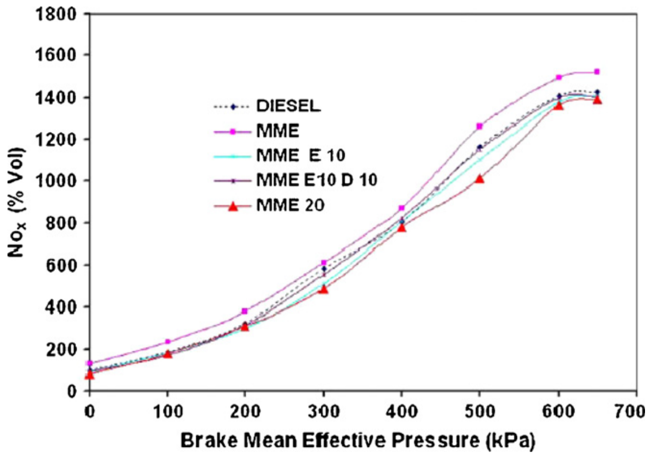

Fig. 8. NO_x emission for ethanol blended biodiesel.

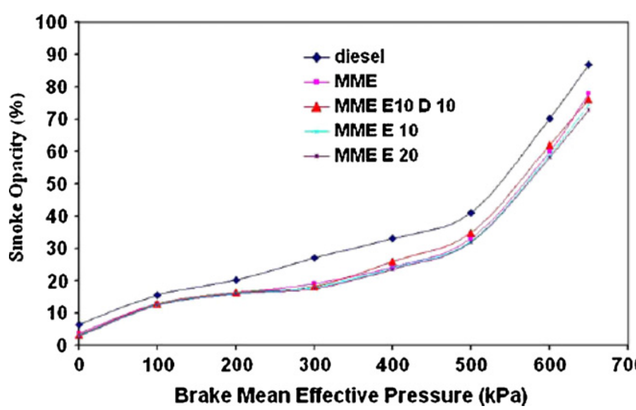

Fig. 9. Smoke opacity for ethanol blended biodiesel.

Fig. 7 shows the HC emission with ethanol blended MME (Mahua biodiesel) were slightly higher than that of the MME level. However, the HC level was on to the lower side than that of the diesel. The MME HC emission on average was 12.4% lower than that of diesel. The reduction in HC emission for ethanol blended biodiesel (E20 and E10) was lower than 9.15% and 5.25%, respectively.

Fig. 8 shows the variation of NO_x for ethanol blended biodiesel. The ethanol blended biodiesel has shown low NO_x emission and was lowest for MME E20 blend.

In Fig. 9 smoke emissions were reduced with the oxygenated fuels and were decreased most with 20% ethanol blended biodiesel.

5. Conclusions

The low-temperature flow properties of biodiesel fuels are less favorable than petroleum diesel fuel. However, blending with additives ethanol, kerosene, methanol, and orange oil improves the cold flow performance. Many anti oxidants have been tried as additives. In summary, addition of short-chain alcohols such as ethanol, isopropanol, and butanol resulted in a moderate improvement in the low-temperature operability of biodiesels. Specific additives for biodiesel remain in their infancy.

With regards to the combustion performance and emission from a diesel engine ethanol seems to be a good additive as the power produced is comparable to the diesel engine operation and has lot of advantage over the biodiesel operation in respect of CO, UBHC, and especially NO_x emissions. Another added advantage of ethanol is that it can be produced from vegetable materials, such as corn, sugar cane, sugar beets, sorghum, barley and cassava, and it has higher miscibility with diesel fuel.

It can conclusively be said that additives are a must for biodiesel production, their storage, transportation in different climatic regions, and usage in a compression ignition engine to have a comparable fossil diesel performance and to realize the dream of using biodiesels to extend the fossil fuel availability.

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